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ELECTRIC POWER FOR NITROGEN FIXATION

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ABSTRACT OF PAPER

Reference is made to propaganda against processes for making nitrates from air by those interested in keeping the Allies depend-

ant on supplies of nitrate from Chili.

A tabular comparison is made of the operations involved in the indirect method and the direct method of fixing nitrogen. indirect method involves the manufacture of carbide of calcium and its combination with nitrogen to form calcium cyanimid, from which ammonia and in turn nitric acid are obtained. direct method merely consists in combining nitrogen and oxygen of the air in the electric arc.

In the direct method electric energy is the only factor, whereas by the indirect much plant of a very diverse and complicated character is required. Also there are difficulties in connection with the platinum catalyst necessary to convert ammonia into nitric acid. It is claimed that the direct method is better because of the simplicity of plant and of operation, and the possibility of working with off peak power. The suggestion is made that a number of plants for making nitrates by the direct arc process should be erected at existing power houses. Keeping the generating plant more fully employed would improve the power factor and reduce costs.

By making nitrate in a number of centers the transportation of same to the explosive factories would be reduced and the risk of interruption of supplies in case of accident or sabotage

would be less than in having a few very large factories.

A diagram is given showing the layout of a battery of byproduct coke ovens with an electric power house worked by the surplus gas and a nitrate from air plant to use the electricity. Figures are given showing that the nitric acid made by such a plant is about the right amount to combine with the ammonia to form ammonium nitrate, a compound in great demand at the present time for explosives.

NE of the most powerful combinations in the world is that connected with the exploitation of Chile Nitrates, and to extend the uses of that material and regulate prices, etc., there is a Chile Nitrate Committee supported by the various interests concerned.

It was created for propaganda work amongst farmers and others, to facilitate the use of nitrate as a fertilizer but since the advent of air nitrates some attention has been given to discrediting the methods of fixing nitrogen from air. This has been

done partly by paragraphs in the press throwing doubt on the financial and technical success of such methods, etc. German influence, working through political clubs and the press, also assisted the Chile nitrate propaganda while at the same time German scientists were being assisted in every possible way to develop air nitrate processes in their own country.

Years before the war, some of us saw that the question of supplies of Chile nitrate for the manufacture of explosives would be an important factor, and in 1911, at the Portsmouth meeting of the British Association, and later at a meeting of the Society of Arts in London, I sounded a note of warning.

To show how differently the Germans tackle these matters, I may say that when the war started, the German government appointed an electrical engineer, head of the Allgemeine Elektricitäts Gesellschaft, to expedite the manufacture of explosives.

On the other hand when the British government started its explosives department a lawyer politician was put in charge, and even afterwards, when a Minister of Munitions was appointed he also was a lawyer politician and had as second in command, a doctor of medicine.

The appointment of politico-legal persons to positions concerned with scientific and engineering matters, has been favorable to Chile nitrate and to German propaganda, in that it retarded developments that would have assisted to make the Allies independent of Chilean supplies.

Even after three and a half years of war, the Allies still remain practically dependent for explosives on supplies which have to be brought thousands of miles. This requires much shipping that might be used for other purposes and also occupies the attention of part of the Navy, in order to keep open the sea routes.

It is to their credit that certain scientists and engineers of this country not only saw the danger, but insisted on the authorities taking action by providing money to establish plants for the manufacture of nitrates.

At the same time, in this country as well as in England, there has been time lost, owing to certain parties maneuvering to obtain the adoption of their own process to the exclusion of others. In so large a field as nitrogen fixation there must necessarily arise numerous improvements in the various processes so that it is not possible today for anyone to gage or forecast their future relative economic values.

This is particularly the case with processes in which electrical energy plays a leading part for it is a sort of ingrained habit of the electrical engineer to simplify and revolutionize existing methods that they eventually become essentially electrical. The whole history of electrical progress, and especially of electrochemistry and metallurgy establishes that fact.

I consider that boards or committees dealing with nitrate problems should be largely made up of engineers who have expert first hand knowledge of electric power conditions and of apparatus, etc. Chemists, pure and simple are, useful but they should not have power to pass upon processes in a field which electrical engineering is capturing so completely as the production of nitrates.

In certain quarters there has been too great a readiness to listen to the tittle tattle of propaganda such as hinted of above.

I feel that the merits of the arc flame process for making nitric acid have not been adequately and sympathetically considered, and this paper is written with the special object of stating them. I wish also to remove the misconception that the arc flame process is dependent on water power and that it can only be installed economically on a very large scale. The matter is one of special interest to electrical engineers because the process is essentially an electrical one.

METHOD OF MAKING NITRIC ACID

One method of producing nitric acid from air which I call the *indirect* method is first to make carbide of calcium, then treat it with nitrogen to form calcium cyanamid, from which ammonia and in turn nitric acid are obtained.

Another method is the *direct* which, consists in combining nitrogen and oxygen of the air directly in the electric arc to form nitric acid.

Those interested in the indirect method have drawn comparisons between it and the direct electric arc process, with the object of showing that the indirect is the better. A tabular comparison of the operations involved in the two processes should thus prove of interest, since it is the only way in which a fair comparison can be made.

It is frequently stated that the amount of electric energy required for a given quantity of nitric acid produced by the indirect process, is less than that required by the direct, and this is put forward as a strong argument in favor of the indirect method. The

only way to compare two operations is to take into account all the factors which go to make up the total cost, and appraise each one at its proper value.

	INDIRECT METHOD Employing Calcium Cyanaploying the Arc Flamid to Make Ammonia and Oxidising the Ammonia to Acid by a Catalyst	
Factories	To make calcium car- 1. To make nitric act bide.	eid.
	 To make cyanamid. To make nitric acid. 	
Operations	Burning limestone. Blowing air through electric arc flame produce nitrous ga	to
	2. Grinding lime. 2. Absorption of gases towers to produce a	s in
	3. Grinding coke or anthracite.	
	 Mixing lime and car- bon in correct propor- tions. 	
	 Making calcium car- bide in electric fur- naces. 	
	 Grinding carbide to fine powder in neutral atmospheres. 	
	7. Making liquid air to produce nitrogen.	
	8. Packing calcium carbide into retorts.	
	 Making calcium cyan- amid by adding nitrogen and by use of electric resistors. 	
	10. Emptying cyanamid from retorts.	
	 Grinding cyanamid to a fine powder. 	
	12. Hydrating cyanamid to rid it of carbide.	
	13. Making superheated steam.	
	 Treatment of cyana- mid with steam in autoclaves to produce ammonia. 	
	15. Oxidation of ammonia to produce weak nitrous gases by means of a catalyst.	
	16 Absorption of gases in	

16. Absorption of gases in towers to produce

acid.

Raw Materials	INDIRECT METHOD 1. Lime. 2. Coke. 3. Carbon electrodes in carbide furnaces. 4. Carbon resistors in cyanamid retorts. 5. Pura pitragen.	DIRECT METHOD 1. Air. 2. Metal electrodes. 3. Water.
Electric Energy for	 Pure nitrogen. Superheated steam. Air. Water. Carbide furnaces. Grinding carbide. Cyanamid retorts. Grinding cyanamid. Heating catalyst. Motors for power, etc., 	1. Arc flame furnaces.
Skilled Labor for	including several cranes. 1. Carbide furnaces 2. Cyanamid retorts. 3. Packing cyanamid. 4. Grinding machinery. 5. Making pure nitrogen. 6. Making ammonia. 7. Catalytic process. 8. Absorption plant.	 Arc flame furnace. Absorption plant.

If two processes are to be compared as regards one factor only, then it may with equal justice be claimed that the electric energy represented by a few motors and lights required for a plant making acid from sodium nitrate, is less than the electric energy required by all other processes for making acid. Such a statement does not prove anything, and yet it is similar to the one put forward by the advocates of the *indirect* process.

Obviously the cost of plant using the indirect method, will be very much greater than that in the case of the direct, for if we assume that the cost of a carbide furnace and its accessories is about the same as that of an air nitrate furnace with its accessories, then, the indirect process embraces in addition:

- 1. A complete plant for making cyanamid.
- 2. A liquid air plant for making pure nitrogen.
- 3. Powerful machinery for grinding the carbide and the cyanamid.
- 4. Steam boilers and autoclaves for making ammonia.
- A complete catalytic plant for oxidizing the ammonia to nitric acid.

In the indirect method it is essential to have all the materials, gases, etc., absolutely pure, for example at the cyanamid works at Odda in Norway it was necessary to carry a pipe up the mountain side so as to ensure a supply of pure air to the liquid air plant.

When carbide is converted into cyanamid some of the formre remains unchanged and in order to obviate danger of explosion a special treatment of the mixture is necessary to ensure a total decomposition of the remaining carbide.

Platinum is usually employed and in order to "reactivate" it, it is necessary to subject it to an acid treatment and eventually to remelt, in which process it is impossible to avoid loss of this expensive metal.

Russia is almost the sole source of platinum, and whilst our Ally, could be depended upon. Today with Germany practically controlling that country, the position is serious. The various allied Governments have had to commandeer platinum as it is essential for several war purposes. With utmost deliberation and foresight the Germans are working to control the worlds storehouse of platinum in the Ural Mountains and any processes which depend upon this rare metal are going to be very seriously handicapped. I consider that those who have had a hand in starting new processes dependent on platinum are very blameworthy. Politicians cannot be expected to know these things but those who do know should inform them.

By the direct method the cost of air is nil, and the cost of water is practically that of pumping. On the other hand, the materials required in the indirect method are very expensive and especially difficult to obtain at the present time. Over three fourths of the cost of working the indirect process is represented in materials liable to price fluctuation. These are now much higher than before the war, and will remain at the higher level after the war.

In the direct method less than one-fifth of the total cost is represented in materials dependent on market rates, and the principal item of cost, namely electric power, will, if anything, tend to come down in price.

The direct method is very simple to operate, whilst the indirect requires much skilled and unskilled labor, and some of the operations are dangerous to health. Therefore, the more labor demands increase, the more will the indirect method be handicapped in this respect. There are many separate links involving exact operating, to make the whole run smoothly and the slightest hitch in connection with any one link necessarily holds up the whole system.

The manufacture of cyanamid has to be carried out in retorts of relatively small size involving much labor to set up, etc. This is to enable the nitrogen gas to penetrate to all parts of the con-

tained carbide. The times of the reaction and the cooling down, etc., are definitely fixed and it is quite impossible to work the process with off-peak power; also should there be an accident or failure of current for a time there is every chance of ruining both the cyanamid retorts and the carbide furnaces.

All nitrate processes have a military bearing as regards preparedness, in which is involved the question of transportation. The heavy and bulky raw materials necessary for the indirect process places it at a serious disadvantage from this point of view. Especially at the present time when the railways are so congested; with the direct process there is no carriage of raw materials.

The indirect process has been strongly advocated in that after the war, cyanamid will be much used as a fertilizer. On the other hand a large number of objections have been voiced against such use, as witness the following extract from a book by Dr. Brion: "Cyanamid cannot be used with a large number of soils such as very sandy or moor soils, or with such soils as tend to become acid. Further it cannot be used for growing tobacco nor for some kinds of fodder. It is useless as a top dressing and can be applied only in dry weather when it must be plowed in at once. Cyanamid attacks the eyes of men handling it."

Whilst some of these objections may have been overcome by making the cyanamid granular and probably also some of them are over-emphasized, it still remains true that cyanamid is by no means as good a fertilizer as nitrate.

The effect of the calcium in calcium cyanamid in the presence of moisture is to cause the reversion of phosphoric acid and therefore it can only be used in limited quantities in a combined fertilizer.

In a legal action in the State of Maine between the Armour Fertilizer works and Ellis Logan, in April, 1916, there was sworn testimony that calcium cyanamid destroyed a crop of potatoes and that not more than 60 to 70 lb. of it should be used per ton of fertilizer. I believe that is only one specific instance of the general situation.

ELECTRIC POWER

As a basic load for a power house the direct arc process presents the advantage that it can be established anywhere, because the raw materials being only air and water, considerations of transportation do not enter into the situation. It is particularly suitable for off-peak or off-season loads, for there is no fused material to solidify, and little to deteriorate in case of stoppage. Some of the furnaces can be switched on and off like an arc lamp, without detriment to brickwork or structural details, or to the process of manufacture.

As there seems to be some doubt as to the possibility of running arc furnaces intermittently on a commercial scale, I would mention that about seven years ago a nitric acid factory was built at Legnano, Italy to utilize 10,000 horse power, especially during the night (see Utilization of Atmospheric Nitrogen by T. H. Norton p. 68). Of course this plant has been considerably extended especially since the war. I am also credibly informed that in Germany there is a very large arc process plant working with off-peak power. At any rate there is no difficulty in doing it, whereas it is impossible to work intermittently with any other method of fixing atmospheric introgen.

In some ways, it is an advantage to run a plant for 8000 or less hours per year, instead of the full number, because the spare time can be conveniently used for renewals and repairs, Less spare plant is thus required and the plant can be operated by two shifts of men.

Because the plants in Norway are very large and only use hydroelectric power, a mythology has grown up, that the arc flame process can only be worked commercially on a very large scale, and with water power. As a matter of fact it is well worth while to build plants of 10,000 kw.

As a matter of fact hydroelectric power may be a disadvantage because of its distance from industrial centers, for either the factory has to be placed in an out of the way position, or else the power has to be transmitted over a long transmission line. I am of the opinion that electrochemical factories should be placed near the power supply, and the ideal position is alongside the power house especially if off-peak power is used.

In a national emergency it is surely better to bring into immediate use all the surplus equipment that already exists, than to start building new power houses, whether hydraulic or steam, and seeing that the direct-arc flame process is suitable for working with off-peak power, I suggest that a number of nitrate plants be forthwith erected at existing power houses.

By erecting say, ten or more nitrate plants of say 10,000 kw. each at power houses in places near where nitrates are required there would be considerable saving in transportation; early de-

liveries of nitrate could be made. Further there would be less risk of temporary interruption of supplies in case of accident or sabotage.

As a matter of fact there are power houses which could easily spare more than 10,000 kw. for over 20 hours a day and through the week end. Also there are power houses fully equipped with steam plant which are now standing idle. In the present crisis they might just as well be brought into use even if the cost of generation is high.

In some power houses the load factor might be doubled and this would have the immediate effect of reducing costs but there has been far too much shilly shallying consideration given to questions of cost. With U-boats on the high seas trying to stop supplies of Chile nitrate, the railways congested with traffic and electrical engineering works making ammunitions, what is the use of discussing power costs. The thing to do is to jump in and make full use of plants already installed.

Recently much has been heard of the suitability of Muscles Shoals, Alabama as a site for the manufacture of nitrates because of the water power which is being developed there, but it will take at least four years to complete these hydraulic works. In the meantime a large steam power house is being built in order that the cynamid process may be put in to early operation This includes a 60,000-kw. turbo generator and should anything happen to it the nitrate plant would be stopped as the various steps of the indirect cyanamid process are so interlocked.

Viewed from this standpoint it would seem to be better in every way to have the manufacture of indispensable materials for explosives manufactured in a number of smaller plants, in widespread centers and by other processes than the indirect.

COKE OVEN AND NITRATE PLANTS

At the present time ammonium nitrate is required in very large quantities for burster charges for shells, torpedoes, mines grenades, etc. This is made from two components, viz., nitric acid and ammonia, both of which are difficult to transport, the first because it is a corrosive acid and the second because in every ton of aqua ammonia there are about $2\frac{1}{2}$ tons of water. An industrial process capable of furnishing electric energy as well as a supply of ammonia would be ideal, and it so happens that this is the case with a regenerative coke oven plant. Half

the total gas made is available and this can be easily turned into electric energy whilst at the same time the nitrogen contained in the coal provides about the right amount of ammonia necessary to combine with the nitric-acid made from the electric energy by the arc flame process.

In order to show how ideal such a system is for making ammonia nitrate, I have prepared the diagram Fig. 1.

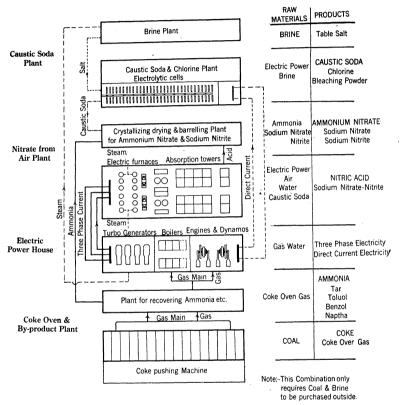


DIAGRAM LAYOUT OF NITRATE FROM AIR PLANT WITH ELECTRIC POWER HOUSE USING COKE OVEN GAS

The scheme provides for a combination of a battery of coke ovens with an ammonia recovery plant together with an electric power house in order to utilize the surplus gas. Alongside the power house, there is an electrochemical plant for the manufacture of nitric acid from air by utilizing the three-phase high-tension current. A nitrate house is provided for the purpose

of combining the ammonia from the coke ovens with the nitric acid from the eletrochemical plant.

It happens that the by-product of the acid factory is sodium nitrate-nitrite, which is made by combining the gases remaining from the acid towers with caustic soda or soda ash. Electrolytic cells may be laid down as shown in the diagram for purpose of making caustic alkali from brine.

It will thus be seen that the complete project requires only two raw materials viz., coal and brine, and on the other hand, the products which can be made are coke and ammonium nitrate together with toluol, benzol, naptha, tar and sodium nitrate-nitrite.

If electrolytic cells are used there are also the products chlorine and bleaching powder. The chlorine can be combined with the benzol to form chloro-benzol which is an important intermediate in the manufacture of dye-stuffs as well as in the manufacture of picric acid.

From the point of view of efficient management, and of elimination of transportation charges, the combination is unique, for the ammonia has only to be piped a few yards to the nitrate house and there is no carriage of acid.

As a cheap supply of coal is indispensable for the project, it would be well to locate the plants at industrial centers where this raw material is readily available and which in all probability would be locations where transportation charges are low.

In order to show what can be done with a coke oven plant the following particulars will be of interest. I take a Koppers type of oven as being the best known.

	Tons	Hours
Quality of Coal	per charge	coking time
Low volatile coal	$13\frac{1}{2}$	18
Mixture containing 80 per cent		
high volatile 20 per cent low		
volatile	$12\frac{1}{2}$	$16\frac{1}{2}$
High volatile coal	$11\frac{1}{2}$	15

A battery of ovens varies in size but we may as well take a round number of 100 for which the average yields are as follows:

Number of ovens	100
Tons of coal per oven	$12\frac{1}{2}$
Hours coking time	16
Total yield of coke	72 per cent
Yield small coal and breeze	5 per cent

Net yield good coke 67 per cent
Ammonium sulphate per ton of coal 25 lb.
Reckoned as ammonia per ton of coal $6\frac{1}{2}$ lb.
Tar per ton of coal
Light oil per ton of coal 3 gal.
Total gas per ton, of coal 11,000 cu. ft.
British thermal units550 per cu. ft.
Surplus gas 55 per cent
Surplus gas per ton of coal6,000 cu. ft.
Such a battery of ovens, each of which distils $12\frac{1}{2}$ tons of
and in 16 hours will don't with

coal in 16 hours, will deal with

$$\frac{100 \times 12.5 \times 24}{16} = 1,900 \text{ tons per day}$$

Assuming 6000 cu. ft. of surplus gas per ton of coal and 550 B.t.u. per cu. ft. the total heat value per hour will be

$$\frac{1900 \times 6000 \times 550}{24} = 260,000,000 \text{ B.t.u.}$$

If employed in gas engines using 13,000 B.t.u. per h.p-hr. the power will be

$$\frac{260,000,000}{13,000}\,=\,20,\!000~\mathrm{h.~p.,~or~say,~14,}000~\mathrm{kw}.$$

If steam boilers and turbines are used instead of gas engines the power will be less so to be on the safe side, we will take the round figure of 10,000 kw.

We will also assume that electric furnaces utilizing 10,000 kwfor a whole year, can produce 6,300 tons of 100 per cent acid. Nitric acid capable of furnishing theoretically 8000 tons of ammonium nitrate as indicated below:-

Allowing 25 lbs. of sulphate of ammonia or $6\frac{1}{2}$ lb. of ammonia per ton of coal, a total consumption of 1900 tons of coal per day should give.

$$\frac{1900 \times 365 \times 6.5}{20,000} = 2250$$
 tons per annum

It will thus be seen that there is plenty of ammonia to combine with the acid made by the surplus gas, even if a higher yield of acid is allowed per kw-yr. and more power is generated.

I purposely leave out of discussion, questions as to types of

nitrogen fixation furnaces and of yields obtained. I may say, however, that it is not right to assume that yields are limited to those usually obtained from certain well known furnaces which must of necessity work with single-phase current.

The amount of ammonium nitrate will be less than the theoretical figure because the efficiency of the reaction is not 100 per cent, also it is usual to convert a certain amount of the gas into sodium nitrate-nitrite. A safe figure would be 7000 tons and at this rate it can be shown that with electric energy at 5 mils per kw-hr. and ammonia at 13 cents a pound, the ammonium nitrate can be made at less than half the price the Government is now paying.

In order to show how large a business the nitrogen industry has become, the following figures (compiled by Dr. Paul J. Fox) give the nitrogen balance sheet for the United States for 1917.

IMPORTED SUPPLIES

	Tons	Tons
	of 2,000 lb.	of Nitrogen
Chile Saltpetre 95 per cent NaNO ₃ .	1,742,540	272,880
Ordinary saltpetre, potassium, nitrate	4,609	645
Ordinary saltpetre and gunpowder		
containing 75 per cent KNO_3	1,500	210
Ammonium sulphate	8,135	1,725
Ammonium chloride	1,073	280
DOMESTIC	SUPPLIES	
Coke oven ammonia—NH ₃	113,760	93,625
Gas works ammonia—NH ₃	12,500	10,288
Calcium cyanamid at 20 per cent		
nitrogen	12,800	10,534
NITROGEN	EXPORTED	
	Tons	Tons
	of 2,000 lbs.	of Nitrogen
Nitric Acid, 15 per cent Nitrogen	486	73
Picric Acid, 18 per cent Nitrogen	26,610	4,790
Dynamite, 12 per cent nitrogen	8,962	1,255
Gunpowder and smokeless powder,		
13 per cent nitrogen	$223,\!270$	29,025
Ordinary saltpetre	875	123

In addition to the above, there are also about 8800 tons represented nitrogen in the following items which are the figures for 1917.

	Value
Loaded cartridges	\$42,000,000
Fuses	34,000,000
Shells and projectiles	74,000,000
All other	202,000,000
Total	253.000.000

It will be noticed that ammonium nitrate is not included in these figures, but I assume it would be about 50,000 tons for 1917.

In Great Britain the consumption of ammonium nitrate is now probably 400,000 tons a year, and the production here will have to be at least as much. To make this, the theoretical proportion of ammonia required is about 85,000 tons and of nitric acid about 315,000 tons.

It will thus be seen that the coke oven plants in the country could supply all the ammonium nitrate required if they were put onto the job.

Until recently most coke oven ammonia was converted into sulphate, but owing to the war demand for nitrate, more and more of it is being made into aqua-ammonia of about 29 per cent strength. In some cases this is being transported many hundreds of miles prior to conversion into ammonium nitrate and since each ton of ammonia necessitates the transportation of about $2\frac{1}{2}$ tons of water, the bearing of this, on the present railway congestion is at once apparent. Tank cars have to be used and they must return empty, so the freight on the actual ammonia carried is extremely high.

There are many coke ovens of the wasteful bee-hive type in operation, which do not recover by-products and the replacement of these by modern coke-ovens would be a great immediate economic gain and meet the war conditions better than the building of large dams for water power.

In the present emergency coke ovens are of great value because they give coke for making steel, gas for power purposes, ammonia for nitrate manufacture, and toluol and benzol for explosives.

After the war ammonium nitrate will be in demand for fertilizer as well as for safety explosives and other purposes. The high percentage of nitrogen which it contains viz., 35 per cent and the ease with which it can be converted into other compounds makes it especially useful for conveying nitrogen in the fixed form over considerable distances.

It is more profitable to make nitrate than sulphate, because, pound for pound, the nitrate contains nearly twice as much fixed nitrogen and the nitrogen commands a higher price per unit when in the form of ammonium nitrate.